Fundamental Aspects of Rapid ClO₂ Delignification of Conventional and Lo-Solids Kraft Pulps

Jian E. Jiang
Ahlstrom Machinery Corp.
Karhula, Finland

A. J. Ragauskas
Institute of Paper Science and Technology
Atlanta, USA
Project Drivers

• Kraft Pulping & Bleaching Evolution
  – Environmentally driven
  – Lower kappa #
  – Improved selectivity & physical properties
  – Improved cost
Research Goal: Improved ClO₂ Bleaching.

- Determine bleaching mechan. of advanced ClO₂ delignification technologies - gas phase and Rapid Do;
- Identify residual lignin fragments resistant to ClO₂ and modify Do or pulping process to enhance lignin reactivity;
- Develop next generation of ClO₂ delignification techn.
Background

• Kraft residual lignin structure
  • Residual lignin structure is influenced by pulping conditions and the extent of delignification

• ClO$_2$ is a selective bleaching agent
  – Residual lignin’s structure will influence its reactivity towards ClO$_2$
Can Residual Lignin Structure Impact Bleachability?

Germgard (1982)
Can Kraft Pulping Impact Bleachability?

Froass et al. (1996)
Objectives

• Determine how the extent of delignification and pulping process variables influence bleachability in a D(EO) delignification sequence employing a modified Do-stage

• Relate the unbleached residual lignin structure and residual lignin reactivity towards ClO$_2$ to bleachability
Experimental Approach

• Bleach pulps in a Rapid Do(EO) sequence and study bleachability parameter (TAC/Δ Kappa #)

• Characterize residual lignin before and after RD(EO) stage

• Relate changes in residual to important bleachability parameters
Pulps Investigated

Loblolly Pine Chips

• Conventional kraft
  – CK 33.0 (32.6 mPa)
  – CK 21.3 (22.6)
  – CK 14.7 (13.3)

• Extended Modified*
  – EK 29.3 (43.4)
  – EK 19.1 (25.5)
  – EK 16.0 (19.2)

*Lo-Solids
Rapid Do Bleaching Protocol

General Principles

- With Good Mixing the bulk of Do delignification occurs in the first 3 minutes.
- Bulk of AOX formation occurs after 3 min.
- Rapid Do delignification kinetics offers opportunity to simplify bleaching equipment:
  - use of high shear mixer and U-tube
### Bleaching Conditions in the RD(EO) Partial Sequence

<table>
<thead>
<tr>
<th>D Stage</th>
<th>EO stage</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>KF</strong></td>
<td>% NaOH</td>
</tr>
<tr>
<td>0.20, 0.05</td>
<td>pHoff: 11.1 ±0.4</td>
</tr>
<tr>
<td><strong>Stirring -</strong></td>
<td><strong>Time</strong></td>
</tr>
<tr>
<td>15 Hz - 30 s</td>
<td>60 min</td>
</tr>
<tr>
<td><strong>Time</strong></td>
<td><strong>Temp.</strong></td>
</tr>
<tr>
<td>static - 30 s</td>
<td>70°C</td>
</tr>
<tr>
<td><strong>Temp.</strong></td>
<td><strong>Consy.</strong></td>
</tr>
<tr>
<td>45°C</td>
<td>10%</td>
</tr>
<tr>
<td><strong>Consy.</strong></td>
<td><strong>Mixer Peg</strong></td>
</tr>
<tr>
<td>10%</td>
<td></td>
</tr>
<tr>
<td><strong>Mixer</strong></td>
<td><strong>O₂ Press.</strong></td>
</tr>
<tr>
<td>Quantum</td>
<td>60 psig (dec 12psi every 5 min)</td>
</tr>
<tr>
<td><strong>Quench</strong></td>
<td><strong>Mixer</strong></td>
</tr>
<tr>
<td>mass Na₂SO₃ added=mass applied ClO₂ x 4.67</td>
<td>Peg</td>
</tr>
</tbody>
</table>
Bleachability of CK & EK Pulps After $^{RD}_o \; \& \; ^{RD}_o(\text{EO}) \; \text{k.f.: 0.05 and 0.20}$

EK exhibits improved bleach.
Bleachability of CK & EK Pulps $^\text{RD}_0$ (EO)

- Consistent & reproducible improved bleachability for EK pulps

<table>
<thead>
<tr>
<th></th>
<th>TAC$\Delta$ Kappa</th>
</tr>
</thead>
<tbody>
<tr>
<td>CK-32.4</td>
<td>0.255</td>
</tr>
<tr>
<td>CK-21.3</td>
<td>0.26</td>
</tr>
<tr>
<td>CK-14.7</td>
<td>0.265</td>
</tr>
<tr>
<td>EK-29.3</td>
<td>0.27</td>
</tr>
<tr>
<td>EK-19.1</td>
<td>0.275</td>
</tr>
<tr>
<td>EK-15.6</td>
<td>0.28</td>
</tr>
</tbody>
</table>

k.f.: 0.20
Chemistry of ClO₂ Delignification

Gierer
Relationship Between Bleachability and Residual Lignin Structure

- Isolate lignin before and after $^R$Do and $^R$Do(EO)
- Characterize Structure

Kraft Pulp
0.10 N HCl 9:1
dioxane:water
Reflux 2 hour

Extracted Pulp

Lignin Extract

lignin is precipitated and freeze-dried
$^1$H-NMR spectroscopy

- Powerful technique to characterize lignin structure
- Structural features discernible
  - Acids
  - Phenols
    - condensed & non-condensed
  - Condensed aromatic structures
  - Methoxy
  - Aliphatic
Methoxy Proton Content for Brownstock, $^R$Do and $^R$Do(EO).

- Brownstock: 29.3
- EK: 19.1
- CK: 15.6

mmol methoxy protons/gr lignin

(R)H

OCH$_3$

OH

mmol methoxy protons/gr lignin

Brownstock

D

D(E+O)

EK: 29.3

EK: 19.1

EK: 15.6

CK: 32.4

CK: 21.3

CK: 14.7
Phenolic Content of Brownstock, $^R$Do and $^R$Do(EO)

mmol phenolics/gr lignin

- $^R$Do big loss
- (EO) minor
Acid Content of Brownstock, $^R$Do & $^R$Do(EO)

- D-stage large increase

mmol Acid units/gr lignin

Brownstock
D
D(E+O)

Pulp

EK:29.3  EK:19.1  EK:15.6  CK-32.4  CK-21.3  CK-14.7
Summary of $^{RD}(EO)$ Studies

- Biggest differences in bleachability for $^{RD}$ and $^{RDo}(EO)$ are with low k.f.
- $^{EK}$ pulps continue to demonstrate improved bleachability at lower kappa number
- $^{CK}$ & $^{EK}$ exhibit differences in residual lignin structure that impact bleachability
- For $^{RD}$ and $^{RDo}(EO)$ bleaching of $^{CK}$ and $^{EK}$ both HexA and lignin structure may influence bleachability
Influence of Brownstock PhOH Lignin on TAC/Δ Kappa

• Typically PhOH increases as kappa # decreases for CK (30 ➔ 20) and PhOH is higher than EK

<table>
<thead>
<tr>
<th>Pulp</th>
<th>TAC/Δ Kappa</th>
<th>Condensed. PhOH²</th>
</tr>
</thead>
<tbody>
<tr>
<td>CK-28</td>
<td>0.21</td>
<td>0.89</td>
</tr>
<tr>
<td>CK-18</td>
<td>0.23</td>
<td>0.99</td>
</tr>
<tr>
<td>EK-29</td>
<td>0.21</td>
<td>0.91</td>
</tr>
<tr>
<td>EK-18</td>
<td>0.22</td>
<td>0.94</td>
</tr>
</tbody>
</table>

¹ 0.20 k.f. calculated after Do(EO)
² mmol/gr lignin

- Froass et al. IPBC 1996
Condensed Phenolics in Brownstock Kraft Pulps Determined by $^1$H and $^{31}$P NMR

Note: less condensed phenolics in EK pulp vs CK pulp.
Relationship between residual lignin structure and pulp bleachability

• Lower kappa number pulps are richer in phenolic content yet harder to bleach

• Bleachability seems to be related to the content of condensed structures and aryl ether linkages
Conclusions

- Residual lignin structure will influence bleaching in a D(EO) sequence
- Pulping conditions influence residual lignin structure and suggests that these conditions can be optimized to enhance and improve ECF bleachability
Acknowledgments

Member Companies IPST
Ahlstrom Machinery Corp.
DOE